

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 14-11-2017		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 15-Feb-2016 - 14-Aug-2017	
4. TITLE AND SUBTITLE Final Report: Structure, Morphology, Property Relationships in Polyisobutylene-Based Triphasic Block Copolymers Containing Hydrophilic/Functional Block Elements			5a. CONTRACT NUMBER W911NF-16-1-0060		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Southern Mississippi 118 College Drive #5157 Hattiesburg, MS 39406 -0001			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 68643-CH.1		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Robson Storey
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 601-266-4879

RPPR Final Report

as of 12-Jun-2018

Agency Code:

Proposal Number: 68643CH

Agreement Number: W911NF-16-1-0060

INVESTIGATOR(S):

Name: Robson Storey
Email: robson.storey@usm.edu
Phone Number: 6012664879
Principal: Y

Organization: **University of Southern Mississippi**

Address: 118 College Drive #5157, Hattiesburg, MS 394060001

Country: USA

DUNS Number: 623335775

EIN: 646000818

Report Date: 14-Nov-2017

Date Received: 14-Nov-2017

Final Report for Period Beginning 15-Feb-2016 and Ending 14-Aug-2017

Title: Structure, Morphology, Property Relationships in Polyisobutylene-Based Triphasic Block Copolymers

Containing Hydrophilic/Functional Block Elements

Begin Performance Period: 15-Feb-2016

End Performance Period: 14-Aug-2017

Report Term: 0-Other

Submitted By: Robson Storey

Email: robson.storey@usm.edu

Phone: (601) 266-4879

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees:

STEM Participants:

Major Goals: The major goals of the project are as follows:

1. Develop new, modular synthetic methods toward PIB-based barrier materials with three different micro-architectures (Figures MG1 and MG 2).
2. Probe the relative importance of composition vs. architecture as a determinant of observed morphology and associated barrier and moisture transmission properties of PIB-based thermoplastic elastomers containing hydrophilic blocks.
3. Characterize barrier performance and water transmission capabilities of synthesized membranes (in collaboration with Natick).
4. Determine the most effective hydrophilic block among several proposed candidates including poly(acrylic acid), poly(ethylene oxide), and poly(ethylene imine).
5. Obtain continued support for this effort through collaboration with Army scientists at Natick and scientists at Defense Threat Reduction Agency (DTRA).

Accomplishments: See "Upload" file for narrative description of accomplishments.

Training Opportunities: Merlin Dartez was selected as a National Research Trainee Fellow for the 2017-2018 academic year. This fellowship is designed to help trainees develop professional skills in an academic setting, such as communication and presentation skills. Through the course of the program, Merlin will receive directed one-on-one sessions with various on-campus communication professionals, aimed at developing his skills as a proficient science communicator. He will also be engaged with community outreach, aimed to improve his skills at effectively communicating to a wide audience.

Results Dissemination: Nothing to Report

RPPR Final Report

as of 12-Jun-2018

Honors and Awards: Merlin Dartez was selected through a competitive process to become a National Research Trainee Fellow, awarded to The University of Southern Mississippi by the National Science Foundation, Award #1449999.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)

Participant: Merlin J. Dartez Jr.

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Jie Wu

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Structure, Morphology, Property Relationships in Polyisobutylene-Based Triphasic
Block Copolymers Containing Hydrophilic/Functional Block Elements**

ARO Final Report

November 14, 2017

PI: Robson F. Storey, The University of Southern Mississippi

Program Manager: Dawanne Poree

Contents:

I Major Goals

II Accomplishments

A. Structure I

- 1. Synthesis of *sec*-benzylic chloride-terminated SIBS**
- 2. Synthesis of azide-terminated SIBS**
- 3. Synthesis of alkyne-functionalized PEtOx**
- 4. Synthesis of alkyne-functionalized PEO**
- 5. Azide-Alkyne cycloaddition of SIBS and PEtOx/PEO**
- 6. Film casting of the terpolymers, TEM analysis of PEO-SIBS films, and moisture vapor transmission rate (MVTR) tests**

B. Structure II

C. Structure III

III Future Work

IV References

I Major Goals

The major goals of the project are as follows:

1. Develop new, modular synthetic methods toward PIB-based barrier materials with three different micro-architectures (Figures MG1 and MG2).
2. Probe the relative importance of composition vs. architecture as a determinant of observed morphology and associated barrier and moisture transmission properties of PIB-based thermoplastic elastomers containing hydrophilic blocks.
3. Characterize barrier performance and water transmission capabilities of synthesized membranes (in collaboration with Natick).
4. Determine the most effective hydrophilic block among several proposed candidates including poly(acrylic acid), poly(ethylene oxide), and poly(ethylene imine).
5. Obtain continued support for this effort through collaboration with Army scientists at Natick and scientists at Defense Threat Reduction Agency (DTRA).

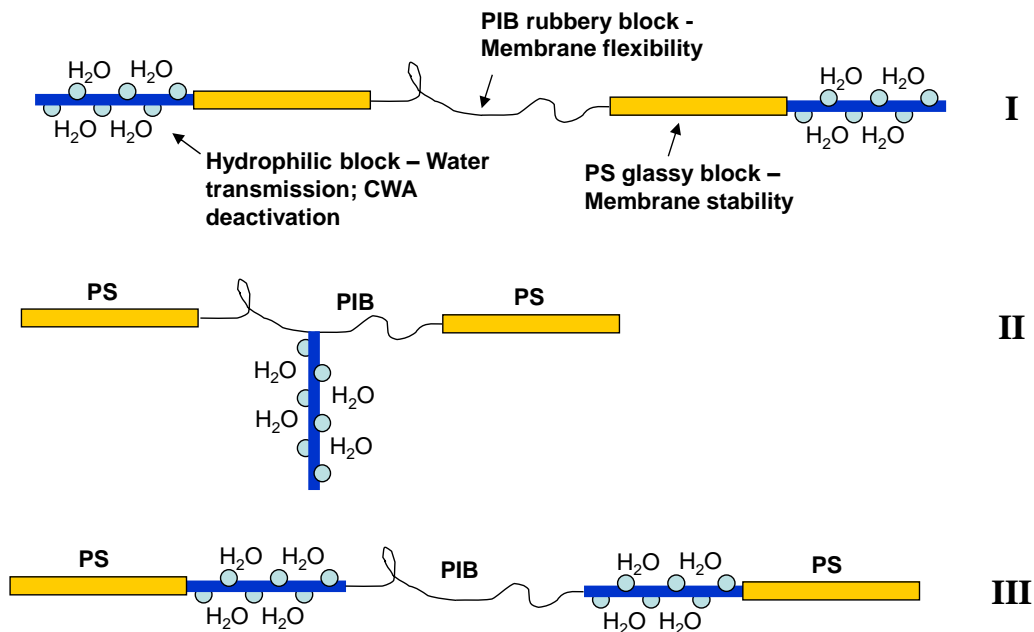
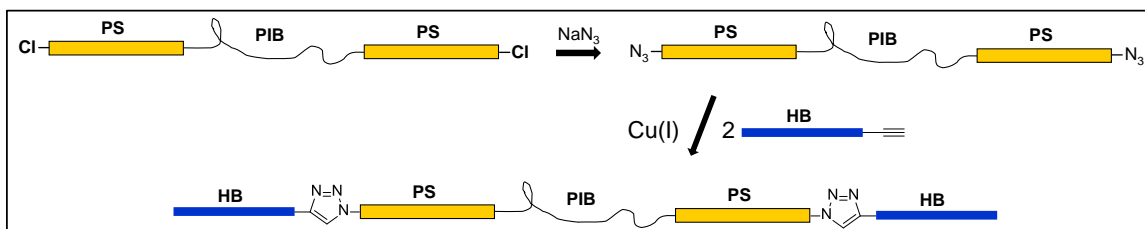
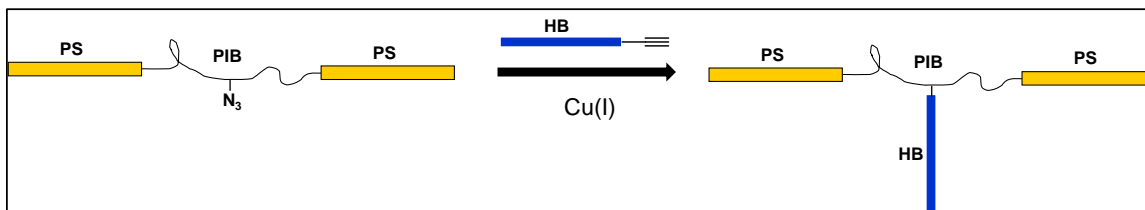


Figure MG1. PIB-based thermoplastic elastomers containing hydrophilic blocks: three micro-architectures proposed.

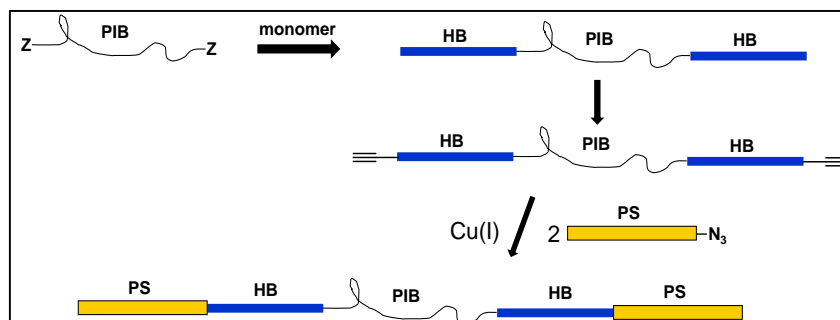
Structure I



Structure II



Structure III (Route for PEO and PEI)



Structure III (Route for PAA)

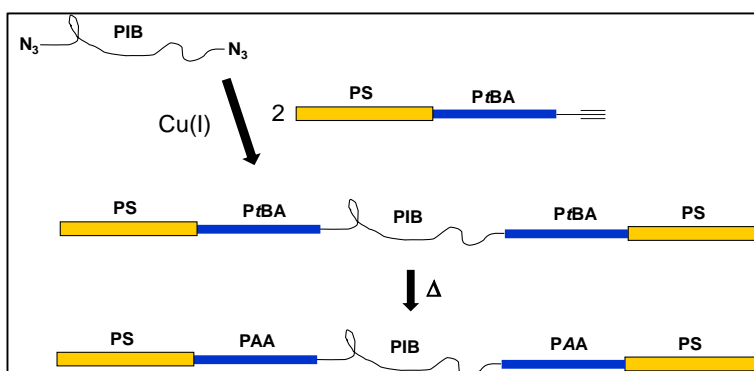


Figure MG2. Proposed synthetic schemes for the three micro-architectures shown in Figure MG1.

II Accomplishments

A. Structure I

1. Synthesis of *sec*-benzylic chloride-terminated SIBS

sec-Benzylic chloride-terminated poly(styrene-*b*-isobutylene-*b*-styrene) (SIBS) was synthesized via living cationic polymerization (LCP) for use as the PS-PIB-PS core of Structure I. The synthesis of SIBS is outlined in Figure A1. The technique of sequential monomer addition was used (isobutylene then styrene), starting from the difunctional initiator, 5-*tert*-butyl-1,3-di(1-chloro-1-methylethyl)benzene (bDCC).

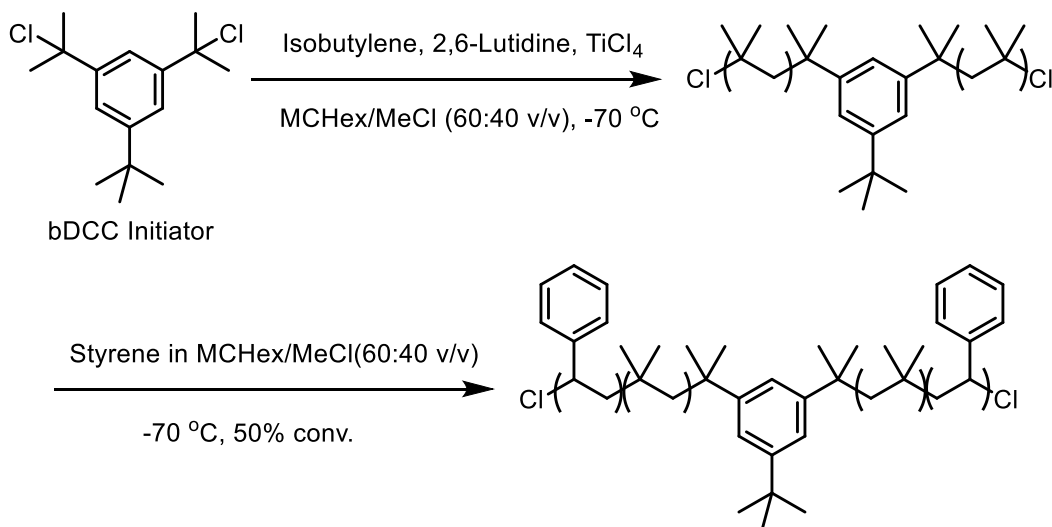


Figure A1. Synthesis of SIBS. *Sec*-Benzylic chloride end groups will be converted to azide end groups for subsequent azide/alkyne click reaction to attach HB block.

The general procedure for synthesis of SIBS was as follows: Reaction was carried out at -70°C within a nitrogen-atmosphere glovebox equipped with a cryostated heptane bath. All glassware were thoroughly cleaned and dried in an oven for 48 h prior to being transferred into the glove box. Styrene was vacuum distilled over CaH_2 no earlier than one day prior to use. The initiator (bDCC) was also dried under vacuum for 4 h immediately prior to use. Methyl chloride and isobutylene were each condensed by passing the gas through a stainless steel coil immersed in the -70°C heptane bath, and collected into separate receiving vessels that were immersed in the bath. The appropriate mass of bDCC was charged to a round-bottom flask, equipped with a mechanical stir rod and ReactIR probe, and immersed in the -70°C bath. Then, methyl chloride and methylcyclohexane were measured into the reactor volumetrically at -70°C , using the methyl chloride charge to rinse all of the bDCC into the reactor. 2,6-Lutidine was

measured into the reactor volumetrically at room temperature. Stirring was activated, and upon temperature equilibration, a reference FTIR spectrum was taken of the reaction mixture. Isobutylene was measured into the reactor volumetrically at -70°C . Several FTIR spectra were acquired and upon thermal equilibration, a charge of TiCl_4 , neat and at room temperature, was added to begin the polymerization. During the IB polymerization, a charge of styrene (50% in methylcyclohexane/methylchloride 60/40 v/v) was prepared in a graduated cylinder and equilibrated in the -70°C bath. Styrene must be added to the reaction mixture as a solution due to the relatively high freezing point. Upon IB reaching 99% conversion (the 887 cm^{-1} peak for the $\text{CH}_2=$ wag of IB reached an asymptotic value), an aliquot was taken for future characterization, and another reference spectrum was taken. The styrene charge was added, and its conversion was monitored by observing the diminution of the $\text{CH}_2=$ wag of styrene at 909 cm^{-1} . The reaction was halted by the addition of excess prechilled methanol at roughly 50% styrene conversion. Early termination at roughly 50% styrene conversion was used to suppress electrophilic aromatic substitution reactions, either intermolecular (leading to coupling) or intramolecular (backbiting).

Upon addition of methanol, the reaction vessel was removed from the glovebox and placed in a hood to warm to room temperature and allow for the evaporation of volatiles. The reaction mixture was then poured into a separatory funnel, and the bottom layer (methanol) was removed. The remaining mixture was concentrated via rotary evaporation and then precipitated slowly into rapidly stirring methanol (1:10 v/v reaction mixture/methanol). The solid polymer was recovered and re-dissolved in minimal methylcyclohexane. The precipitation was repeated a total of three times, at which point the solid polymer was dissolved in a large amount of methylcyclohexane. The resulting solution was washed with DI water three times. The solution was then dried with anhydrous MgSO_4 and filtered. It is more convenient to store SIBS in a solution of known concentration in methylcyclohexane rather than as a dry polymer. The NMR spectrum and GPC traces obtained of representative samples are shown in Figures A2 and A3, respectively.

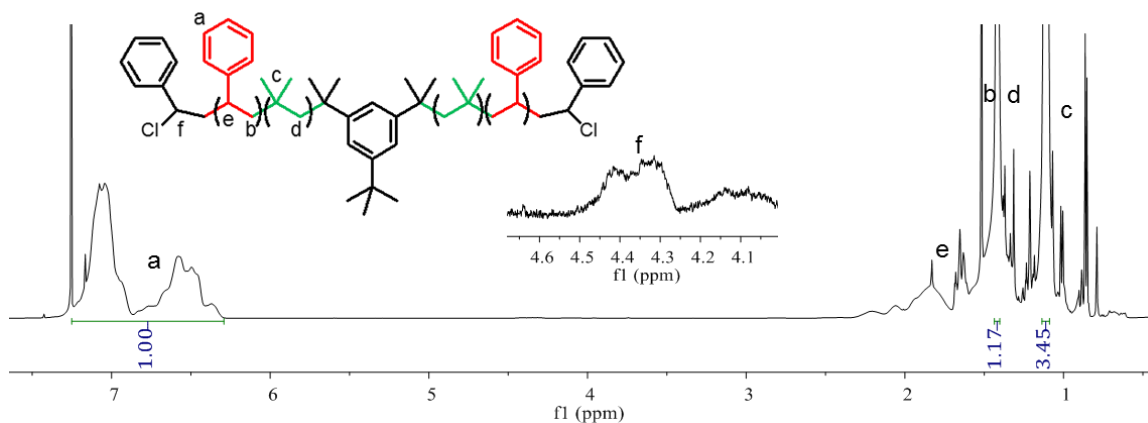


Figure A2. ^1H NMR spectrum (CDCl_3 , 600 MHz) of *sec*-benzylic chloride-terminated SIBS (Entry 1, Table A1).

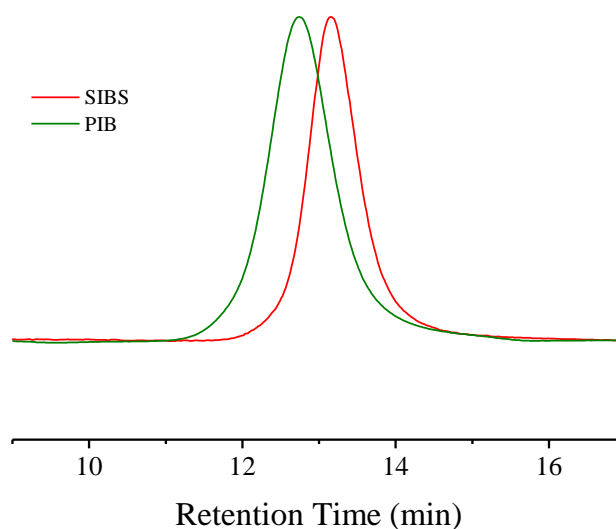


Figure A3. GPC refractive index trace of chloride-terminated PIB and *sec*-benzylic chloride-terminated SIBS (Entry 3, Table A1).

In Figure A2, the methine proton adjacent to the *sec*-benzylic chloride end groups can be observed at 4.2-4.5 ppm. From Figure A2, the number average molecular weight (M_n) of the SIBS polymer can be calculated. We first obtain the molar ratio of isobutylene to styrene repeat units using either eq (1) or (2), which utilize the integrated areas of the peaks of either the PIB backbone methyl groups (c) or methylene groups (d), respectively.

$$r = \frac{A_c}{A_a} \times \frac{5}{6} \quad (1)$$

$$r' = \frac{A_d}{A_a} \times \frac{5}{2} \quad (2)$$

In equations 1 and 2, r and r' are ratios of repeat units of isobutylene to styrene in one SIBS molecule, A_a , A_c , and A_d represent integration of peaks a, c, and d, respectively. The overall number average molecular weight of the SIBS copolymer, $M_{n,SIBS}$, is then calculated using eq (3),

$$M_{n,SIBS} = M_{n,PIB} + \frac{M_{n,PIB}}{M_{IB} \times r} \times M_S \quad (3)$$

where, $M_{n,PIB}$, M_{IB} , and M_S represent the molecular weight of the PIB centerblock, isobutylene repeat unit, and styrene repeat unit, respectively. An equation analogous to equation (3) may be obtained using r' instead of r . The molecular weight of the PIB centerblock is in this case 20,000 g/mol, calculated from the monomer to initiator ratio used in the polymerization. The calculated molecular weight of the synthesized SIBS polymer using NMR data in this way is 32,900 g/mol (using r) and 32,700 g/mol (using r').

The number average molecular weight and PDI calculated from GPC data are 34,800 g/mol and 1.13, respectively. The error between M_n data from NMR and GPC is about 5%. Overall, the experimental molecular weight is slightly higher than theoretical target of 30,000 g/mol, which is most likely attributable to a styrene monomer conversion somewhat higher than the target value of 50%.

A series of SIBS with various molecular weights was synthesized, and the GPC data obtained are shown in Table A1.

Table A1. GPC data for various SIBS batches

Entry	PIB (g/mol)	PS (g/mol)	PDI
1	20,000	14,800	1.13
2	7,990	5,410	1.08
3	19,980	14,490	1.06
4	52,290	20,030	1.10
5	23,900	12,020	1.06

2. Synthesis of azide-terminated SIBS

The *sec*-benzylic chloride end groups of SIBS were converted to azide end groups to enable coupling of the SIBS core to various alkyne-terminated hydrophilic blocks. Azide-terminated SIBS was synthesized by reaction of the *sec*-benzylic chloride-terminated SIBS with sodium azide at 100°C in 50/50 (v/v) methylcyclohexane/DMF, in the presence of tetrabutylammonium bromide (TBAB) as phase transfer catalyst. This

solvent combination provides a homogeneous reaction medium at the reaction temperature and a phase-separated medium at room temperature, which facilitates separation of the azidized SIBS product from excess NaN₃, NaCl byproduct, and catalyst. Reaction was performed at 100°C for 48 h, and the NMR spectrum of a representative sample is shown in Figure A4. The disappearance of the *sec*-benzylic chloride methine peak (4.2-4.5 ppm) and appearance of azide methine peak (3.8-4.1 ppm) indicate that the azidation was successful.

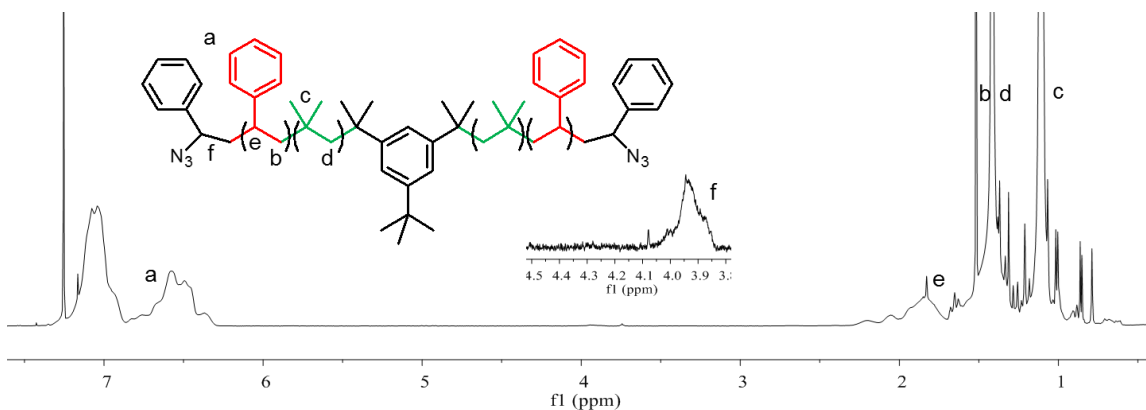


Figure A4. ¹H NMR spectrum (CDCl₃, 600 MHz) of azide-terminated SIBS.

3. Synthesis of alkyne-functionalized PEtOx

Alkyne-terminated poly(ethylene imine) is a hydrophilic block of interest for Structure 1. Poly(2-ethyl-2-oxazoline) (PEtOx) was synthesized as a precursor to PEI. The alkyne terminus was fitted to PEtOx by using propargyl tosylate as a cationic ring opening polymerization initiator for 2-ethyl-2-oxazoline monomer.

Propargyl tosylate was prepared as follows: A reaction flask equipped with a magnetic stir bar was cooled to 0°C in an ice bath under a N₂ purge. The flask was then charged with appropriate masses of propargyl alcohol, tosyl chloride, and Et₂O. The reaction mixture was allowed to stir vigorously under N₂ for 30 min. Then, NaOH was added to the reactor in 6 portions over the course of 1 h. The resulting mixture was allowed to warm to RT; the N₂ purge was removed, and mixture was left to react overnight under vigorous stirring. The resulting suspension was poured into a large excess of cold Di H₂O. The resulting mixture was poured into a separatory funnel, and the aqueous layer was removed and extracted with 3 100mL portions of Et₂O. All of the ether layers were combined, dried over MgSO₄, and concentrated *in vacuo* to yield a yellow oil.

EtOx was distilled over CaH₂ under reduced pressure (30°C @ 0 torr) one day prior to the polymerization reaction. To an oven-baked reaction vessel were charged appropriate amounts of EtOx monomer, propargyl tosylate, and anhydrous acetonitrile. Six microwave vials were charged with roughly 25 mL of masterbatch solution and a

magnetic stir bar, and were capped. The reaction temperature was set to 140°C, and each reaction time was set as per the reaction rate constant obtained from literature. Upon complete reaction, a charge of water was added. The polymerization mixture was vacuum stripped, diluted with CHCl₃ and precipitated into cold ether from CHCl₃ three times. After final vacuum stripping, the product was obtained as a white powder. Large batches (> 10g) need to be freeze dried to remove residual water.

Figure A5 shows a NMR spectrum of a representative PEtOx produced in this work. The propargyl proton, d, is convoluted with the methylene protons of the side chain, and therefore d cannot be used to quantify the degree of polymerization by NMR. However, the methylene protons of the propargyl group, a, can be integrated relative to the b protons to provide degree of polymerization. The sample shown in Figure A5 had degree of polymerization by NMR of 57.4, which corresponds to a molecular weight of 5,690 g/mol.

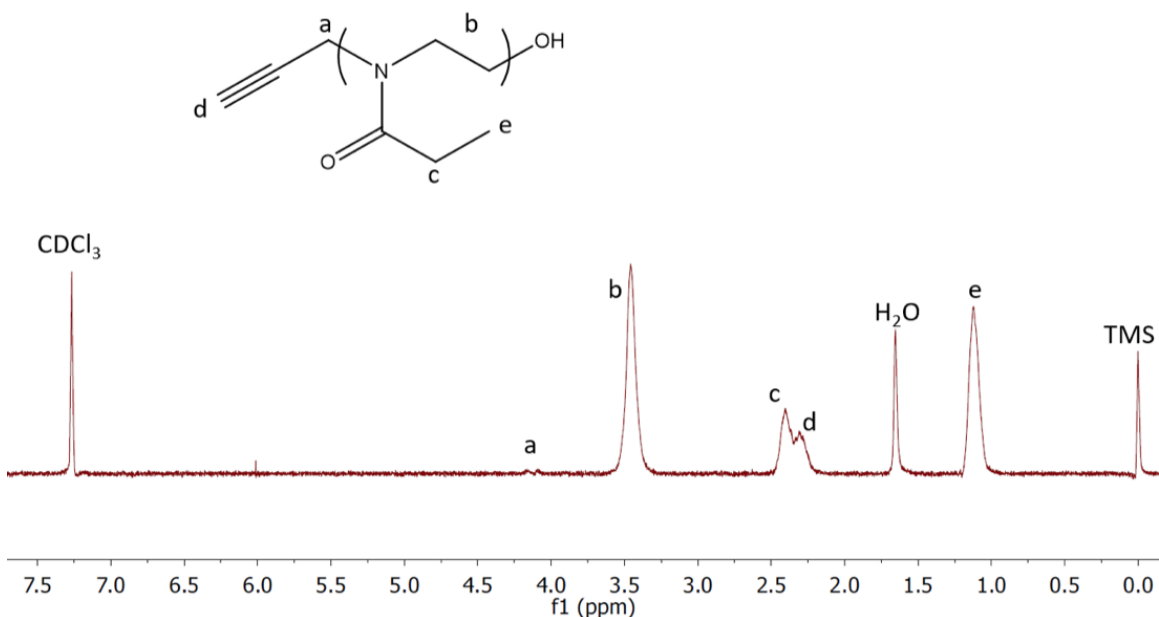


Figure A5. ¹H NMR spectra (CDCl₃, 300 MHz) of alkyne-PEtOx.

4. Synthesis of alkyne-functionalized PEO

Synthesis of alkyne-functionalized PEO for structure I was relatively straightforward, from commercial hydroxyl-terminated PEO. We obtained PEO of about 5,000 g/mol, fitted with one methoxy terminus and one hydroxyl terminus. As shown in Figure A6, this polymer was reacted with propargyl bromide in a Williamson ether synthesis carried out at 50°C and catalyzed by KOH.

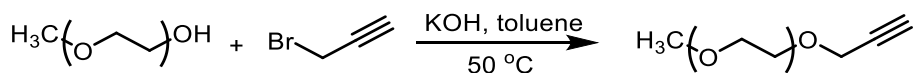
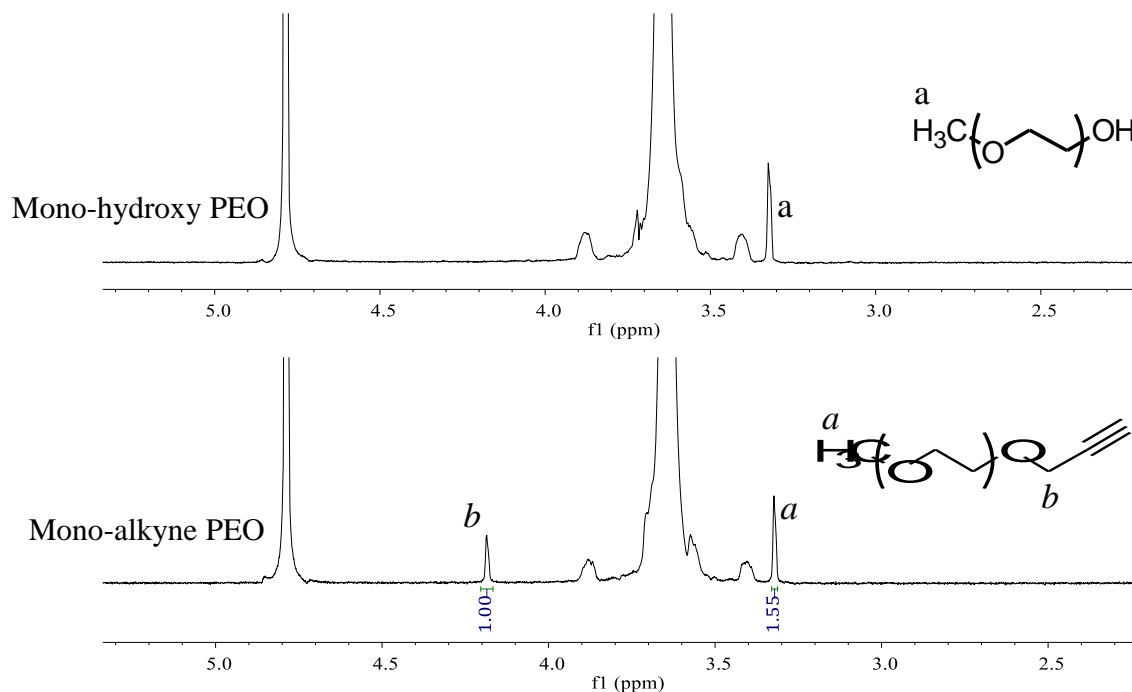


Figure A6. Synthesis of alkyne-functionalized PEO.

The ^1H NMR spectra of the PEO before and after reaction with propargyl bromide are shown in Figure A7. The reaction was successful, as indicated by the appearance of the methylene protons of the propargyl moiety at about 4.2 ppm; integration of this peak indicated a propargyl functionality of about 97 mol%.



Mol conversion: $(1.00 \times 3/2) / 1.55 \times 100\% = 96.7\%$

Figure A7. ^1H NMR spectra (D_2O , 23°C) of PEO before (top) and after (bottom) reaction with propargyl bromide.

5. Azide/alkyne cycloaddition of azide-terminated SIBS with alkyne-terminated HB blocks

Structure I terpolymers were constructed by azide/alkyne cycloaddition “click” reaction of the alkyne-terminated HB blocks (PEI and PEO) with azide-terminated SIBS.

PEO-SIBS synthesis. In order to prevent the copper(I) catalyst from being oxidized in the air, azide-terminated SIBS, alkyne-terminated PEO, sodium ascorbate, Cu(I)Br , N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA), THF, and a stir bar were first sealed in the reaction flask with rubber septa in the nitrogen-atmosphere glovebox. The flask was then transferred out of the glovebox into an oil bath. The flask was then equipped with a condenser, and stirring was started, and the mixture was sparged with argon for 15 min. The reaction was performed at 70°C under argon protection (the needle connecting a balloon with argon) for 48 hr. The mixture was then passed through

alumina and Dowex 88 cation-exchange resin to remove copper catalyst. Workup of the crude product was at first difficult, because the PEO blocks greatly increased the hydrophilicity of the polymer, which made it soluble in methanol and caused formation of an emulsion upon mixing with water. After experimenting with different solvent/non-solvent combinations, it was found that the polymer could be purified and isolated by precipitation from a methylene chloride solution into excess water:methanol (v:v = 1:1). NMR spectrum and GPC traces obtained for one of the samples are shown in Figures A8 and A9, respectively.

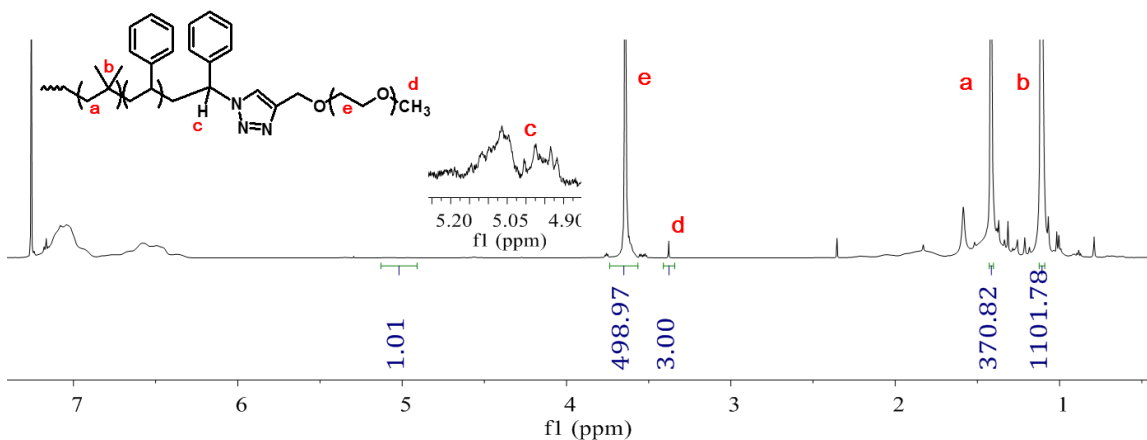


Figure A8. ^1H NMR spectrum (CDCl₃, 600 MHz) of PEO-SIBS.

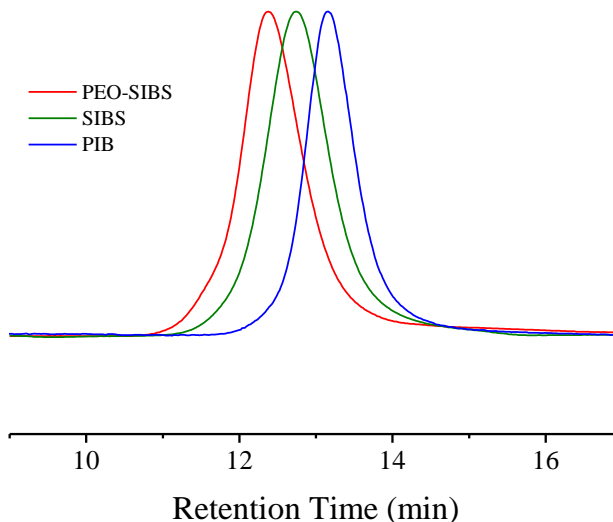


Figure A9. GPC refractive index traces of PEO-SIBS.

The number average molecular weight values (g/mol) calculated from GPC were 19,980 for the PIB block (44.9 wt%), 14,490 for both PS blocks combined (32.6 wt%), and 10,020 for both PEO blocks combined (22.5 wt%). The overall M_n and dispersity index of the PEO-SIBS were 44,490 and 1.12, respectively. As shown in the NMR spectrum,

the azide methine peak (originally at 4.2-4.5 ppm) has disappeared, and PEO backbone peak (3.64 ppm), PEO chain end methyl peak (3.38 ppm), and triazole peak (5.1 ppm) can now be observed. Furthermore, the ratio of the area of the peak at 1.1 ppm (which corresponds to the PIB methyl groups) to the area of the peak at 3.38 ppm (which corresponds to the PEO end methyl group) is 367.3 (1101.78/3), which is closely matched to the theoretical value (351). The other integration values are also close to theoretical values.

PEI-SIBS synthesis.

To a reaction flask were charged appropriate amounts of vacuum dried N₃-SIBS-N₃ (Entry 5, Table A1), alkyne-PEtOx, and freshly distilled THF. The reaction mixture was sparged with dry N₂ for 4 h, and then the flask was brought into the glovebox. To the reaction were charged CuBr and PMDETA. The reaction mixture was removed from the dry box and maintained at 60°C for 72 h under a blanket of N₂. After the reaction was allowed to cool to RT, it was exposed to air, effectively killing any remaining catalyst. The reaction mixture was concentrated *in vacuo*, and the residue was suspended in methylene chloride. The suspended residue was precipitated dropwise into rapidly stirring, near-boiling water (i.e., steam stripped). The water-swollen polymer was then collected, pressed, and kneaded in acetonitrile, and then the resulting crumb was re-suspended in methylene chloride. Steam stripping was then repeated two more times. After the final steam stripping, the polymer was pressed and kneaded in acetonitrile, then broken up into small fragments. These fragments were suspended again in dry acetonitrile and stirred for 48 h (after 24 h, the acetonitrile was refreshed) to extract any residual homo-PEtOx and any water coordinated within the terpolymer. After extraction, the polymer was collected and vacuum dried for 72 h to yield PEtOx-SIBS as a white solid.

To a reaction vessel was charged PEtOx-SIBS dissolved in THF, and to this mixture were added NMP, 2 mL of concentrated H₂SO₄, and 10 mL of H₂O. The reaction was allowed to run overnight at reflux. After the reaction was complete, the mixture was allowed to cool to RT, and 20 mL of H₂O were added (until the mixture became very cloudy). The pH was checked and found to be acidic; thus KOH_(aq) was added dropwise until the solution became neutral. The reaction mixture was concentrated under vacuum, redissolved in MeCl₂ and precipitated three times via vacuum stripping to yield PEI-SIBS as a white solid. Due to the presence of free amine functions, PEI-SIBS cannot be characterized by GPC. Proton NMR spectra of PEtOx-SIBS and PEI-SIBS are shown in Figures A10 and A11, respectively. GPC traces of the PIB centerblock (Entry 5, Table A1), corresponding SIBS, and final PEtOx-SIBS are overlaid in Figure A12.

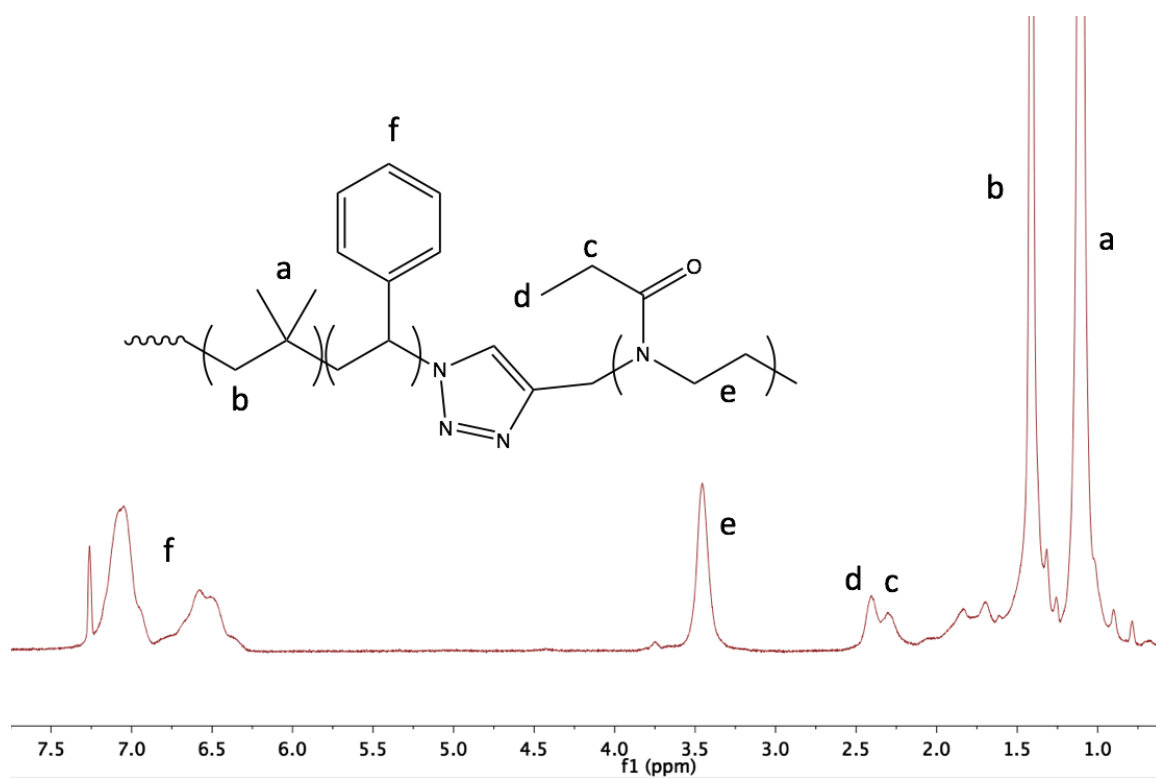


Figure A10. ¹H NMR spectrum (CDCl₃, 600 MHz) of PEtOx-SIBS.

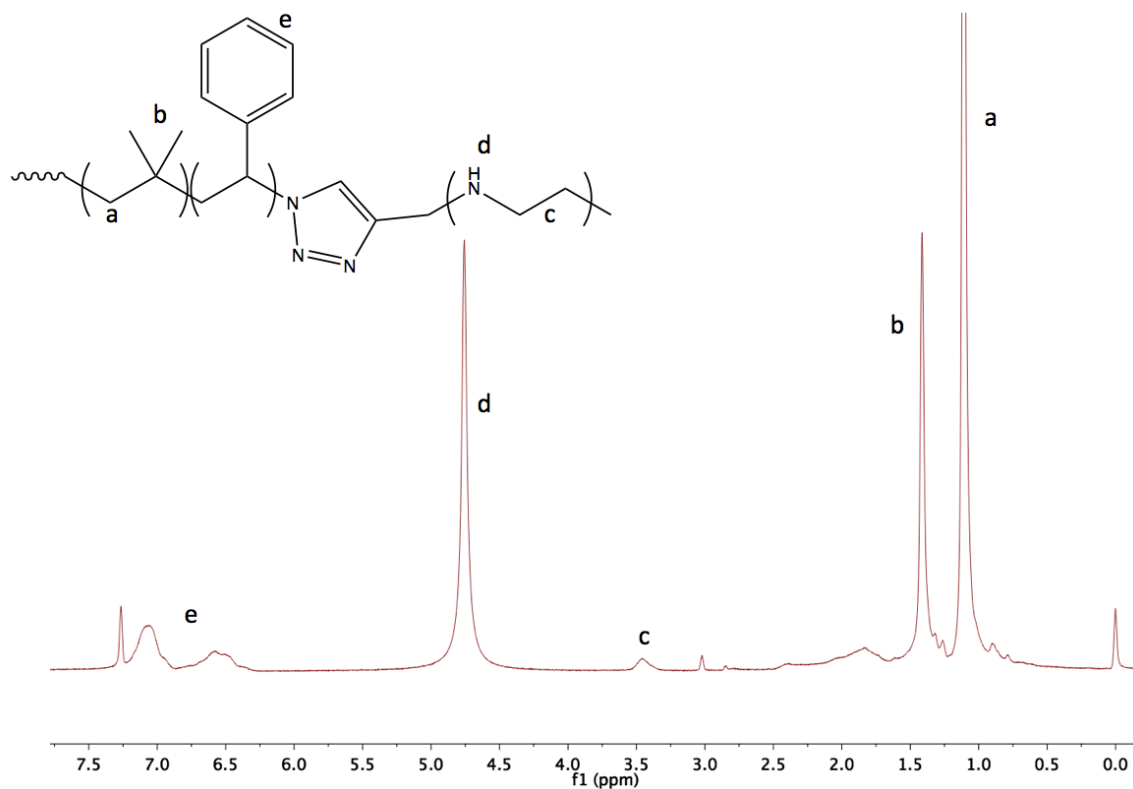


Figure A11. ^1H NMR spectrum (CDCl_3 , 600 MHz) of PEI-SIBS.

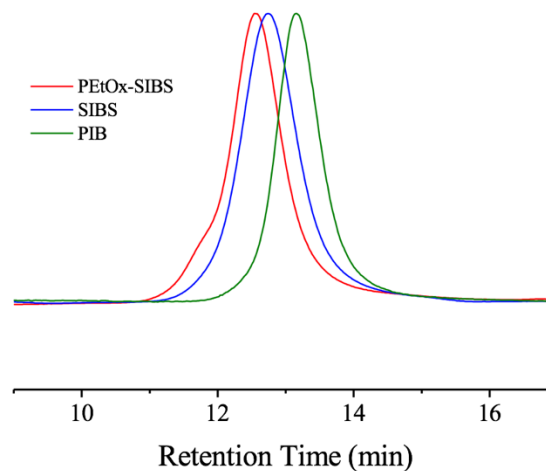


Figure A12. GPC refractive index traces of PEtOx-SIBS.

The number average molecular weight values (g/mol) calculated from GPC were 23,900 for PIB block (51.7 wt% pre-hydrolysis and 58.7 wt% after), 12,020 for PS blocks combined (26.0 wt% pre-hydrolysis and 29.6 wt% after), 10,345 for PEtOx blocks combined (22.3 wt% pre-hydrolysis) and PEI blocks combined (11.7 wt% post-hydrolysis). The total M_n and dispersity index of the PEtOx-SIBS were 46,265 g/mol and 1.073,

respectively. The weak high molecular weight shoulder in the GPC trace of PEtOx-SIBS is attributed to coupling involving transamidation reactions between the main chain oxazoline units. The total M_n for PEI-SIBS was 40,700 g/mol after hydrolysis, determined by NMR since PEI-SIBS cannot be characterized by GPC. As shown in the NMR spectrum, azide methine peak (originally at 4.2-4.5 ppm) disappeared and the PEtOx main chain peaks (3.51 ppm), and side chain peaks (2.4 ppm) can be observed. Upon hydrolysis, the side chain proton peaks (2.5 ppm) decrease significantly in intensity and the peak for the amine proton can be observed (4.75 ppm). It is difficult to obtain precise quantitative data from the spectrum obtained from PEI-SIBS. Due to its high degree of hydrophilic elements it is difficult to completely solubilize the material, and it is believed that not all protons are fully relaxing (hence the decrease in peak intensity of the main chain (3.5 ppm) protons upon hydrolysis). Furthermore, the peak at 4.75 ppm is artificially broadened due to a high degree of water coordination. More work needs to be done to definitively quantify the degree of hydrolysis via NMR; for now, we can conclude that the degree of hydrolysis is nearly quantitative, due to the disappearance of the side chain proton peaks. Using the following relationship, we can predict the molecular weight of the PEI blocks, if we know the original weight of the PEtOx blocks and assume near quantitative conversion.

$$Mn_{PEtOx} = \frac{99.13}{43.07} (Mn_{PEI} - 56.06) + 56.06 \quad (4)$$

6. Film casting of the terpolymers, TEM analysis of PEO-SIBS films, and moisture vapor transmission rate (MVTR) tests

Film casting and TEM analysis of PEO-SIBS (Mw 44,490). Films were cast from approximately 10% (w/v) polymer solutions using THF solvent. Solutions were poured into Teflon pans and tightly covered with aluminum foil in which several holes had been punched with a syringe needle to allow for slow vapor release and better film formation. Films were formed over a period of 6–8 d at 60°C and then vacuum-annealed for 12 d at 110 °C. After annealing at high temperature under vacuum, the films darkened and were observed to contain bubbles.

Specimens were prepared for TEM inspection by cryo-sectioning at an angle of 6 degrees relative to the knife at a speed of 1.5–3.5 mm/s on a Reichard-Jung Ultracut E microtome. The microtome chamber, diamond knife, and samples were kept at -90°C. Ultrathin sections approximately 70 nm thick were placed on copper TEM grids. The specimens were stained with RuO₄ vapor in a Petri dish for 4 min followed by OsO₄ solution to provide contrast for imaging the microphase separated morphology. The sections were viewed using a Jeol 2100 T electron microscope operating at 200 kV or a Zeiss 900 TEM operating at 80 kV. Images obtained are shown in Figure A13.

The images suggest a lamellae structure. Though the resolution is low due to samples being too thick, and the triphasic morphology cannot be identified. Further investigation will be performed.

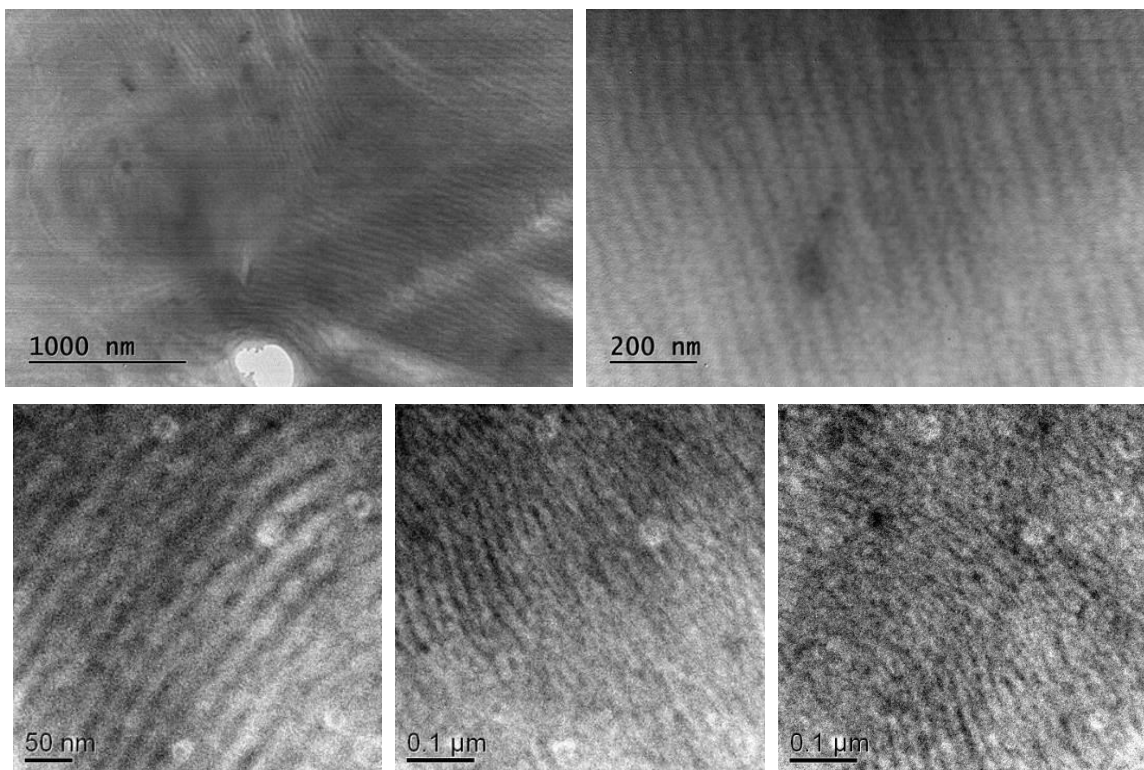


Figure A13. TEM images of the PEO-SIBS film.

Moisture vapor transmission rate test of PEO-SIBS film (Mw 45,000 g/mol). The water permeability of the PEO-SIBS film was then tested. To a Gardco 10 cm² perm cup was added an appropriate amount of DI water. A 0.23 mm thick sample of PEO-SIBS film pre-cut to the outside dimensions of the clamp ring was placed on the top surface of the cup, and sealed against the cup surface with gaskets. The assembly was then weighed and placed in a desiccator. Periodic weighing was performed, and the weight loss vs time plot was obtained as shown in Figure A14.

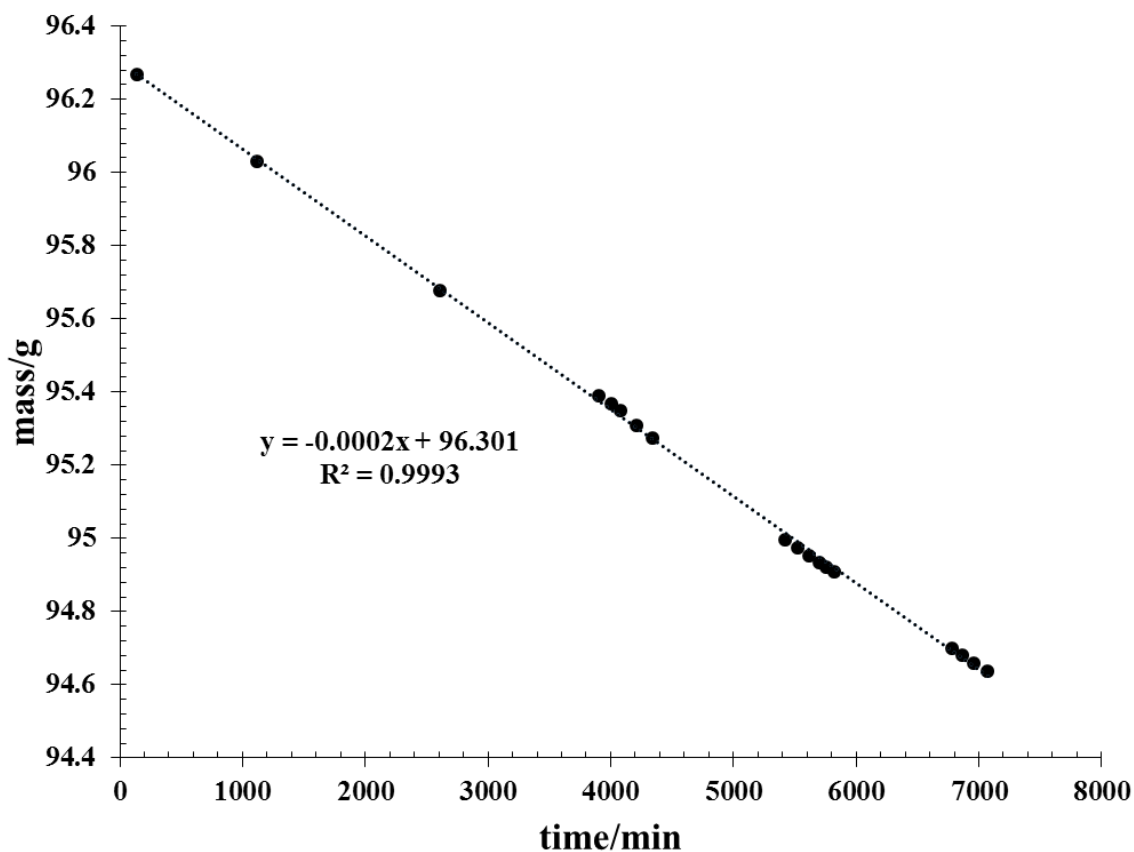


Figure A14. Weight loss curve of PEO-SIBS film for the MVTR test at 18 °C.

From the slope of the curve, the water permeability of the film can be calculated as follows:

$$\text{Permeability} = \frac{m \cdot T}{t \cdot A \cdot \Delta P_v} = 1.779 \times 10^{-4} \text{ g/h} \cdot \text{m} \cdot \text{mmHg}$$

Where m/t represents the mass loss over time (the slope of the plot), T represents thickness of the film, A is the area of the sample exposed to moisture (the area of the perm cup opening, 10 cm²), and ΔP_v represents the water vapor pressure difference at 18 °C (15.5 Torr or 2.07 kPa). Compared to the data of the previous work,^{1,2} the permeability increased an order of magnitude.

Film casting of PEI-SIBS (Mw 40,693 g/mol). Films were cast from approximately 10% (w/v) polymer solutions using THF solvent. Solutions were poured into Teflon pans and tightly covered with aluminum foil. Then, several holes were punched in the foil with a syringe needle to allow for slow vapor release and better film formation. Films were formed over a period of 6–8 d at 60°C and then vacuum-annealed for 12 d at 110°C. The production of homogeneous, thin films of PEI-SIBS for TEM analysis has yet to be

completed. The films show dark spots (unknown impurities) as well as varying sample thickness throughout the sample. Further work must be carried out to produce usable films.

B. Structure II

There is nothing to report on Structure II at this time.

C Structure III

1. Synthesis of primary bromide-terminated PIB

As shown in Figure MG2, the synthesis of Structure III requires difunctional PIB carrying various terminal functionality depending the intended hydrophilic block, e.g. azide functionality is required by PAA. As a modular approach, we have prepared PIB masterbatches (~100 g each) carrying primary bromide termini (Br-PIB-Br) using LCP in conjunction with alkoxybenzene quenching. Primary bromide is nearly an ideal functional precursor due to its ready conversion to many different functionalities via nucleophilic substitution. We have prepared several masterbatches with molecular weights ranging from about 5,000 – 30,000, as summarized in Table C1.

Table C1. Summary of Br-PIB-Br masterbatch molecular weights and distributions from NMR and GPC.

Mn, NMR (g/mol)	Mn, GPC (g/mol)	PDI	End Group
6,497	5,933	1.09	Primary Br
11,190	11,146	1.07	Primary Br
24,589	25,490	1.04	Primary Br
31,658	31,760	1.05	Primary Br

A representative procedure for the synthesis of Br-PIB-Br (Entry 3, Table C1) was as follows: polymerization was carried out at -70°C in an inert atmosphere dry box equipped with a chilled pentane bath. Isobutylene consumption was monitored via real-time ATR-FTIR (ReactIR). A 1L 4-neck flask, equipped with a glass stirring rod/Teflon stirring paddle and a ReactIR probe, and placed in the -70°C pentane bath. To the reactor were charged 218 mL Hexane, 327 mL methylchloride, 175 mL isobutylene, and 0.25 mL 2,6-lutidine, and 1.44 g bDCC. The reactor contents were allowed to cool to -70 degrees Celsius, at which time 1.85 mL TiCl₄ (neat and at room temperature) was added to the reactor. Upon reaching essentially 100% monomer conversion (~2h), 3.55 mL of 3-

bromopropoxybenzene and 2.54 mL TiCl_4 were added to the reaction, and the contents were allowed to stir overnight. The polymerization catalyst was then destroyed by the addition of 10 mL methanol and the reaction was allowed to warm to room temperature in a fume hood, during which time the methyl chloride was evaporated away. The resulting polymer solution was separated from the lower methanolic layer and precipitated into excess methanol. The solvent was decanted, and the sample was redissolved in MCHex, washed with water 3 times, and dried overnight using anhydrous magnesium sulfate. After filtration, the solvent was then vacuum stripped.

Figure C1 shows GPC traces for the four PIB samples of Table C1. All four traces display a mono-modal, symmetrical distribution. GPC molecular weights, determined by MALLS detection are listed in Table C1.

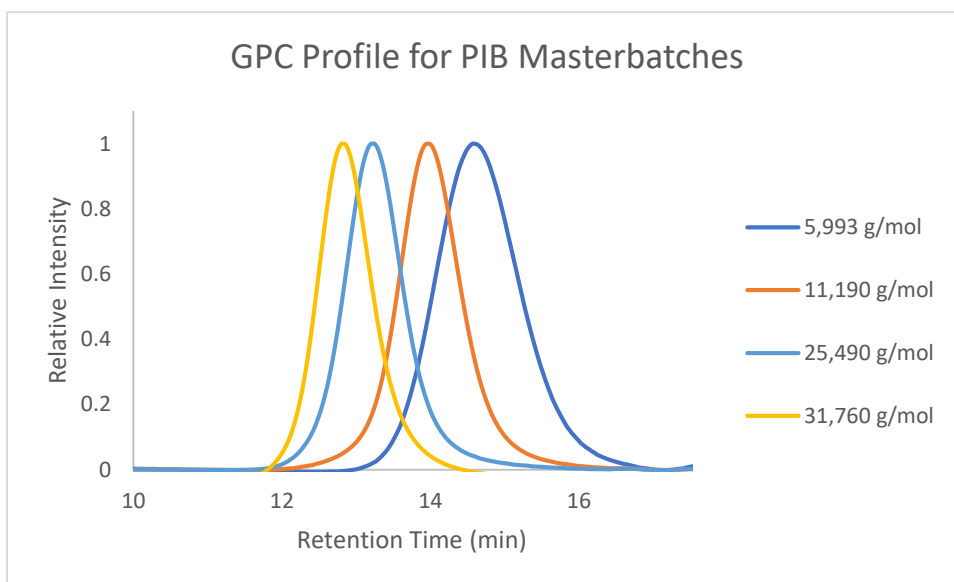


Figure C1. GPC traces for Br-PIB-Br samples of Table C1.

NMR spectra of the Br-PIB-Br samples of Table C1 are shown in Figure C2. The resonances characteristic of the (3-bromopropoxy)benzene quencher moiety are visible in each of the spectra and are labeled relative to the structure shown in the figure.

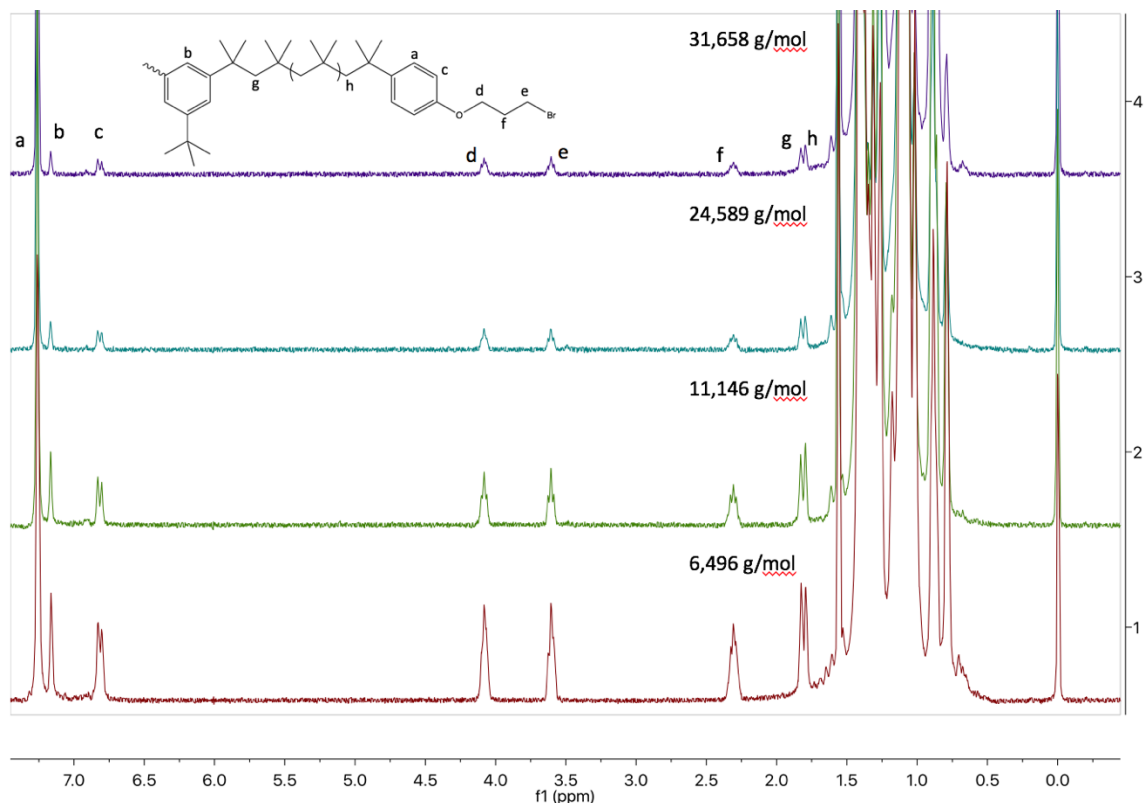


Figure C2. ^1H NMR spectra of Br-PIB-Br samples of Table C1.

III Future Work

A. PEO-SIBS

Efforts to synthesize higher molecular weight PEO blocks via anionic polymerization are being devoted. More TEM analysis will be performed to obtain images with better resolution so that the morphology of the tri-phasic system can be identified. The initiator of structure II is also being synthesized.

B. PEI-SIBS

More work needs to be done to effectively quantify the degree of conversion from PEtOx-SIBS to PEI-SIBS. We believe the problems with quantifying conversion using NMR data lie with solubility of the polymer; more solvents (or solvent combinations) need to be investigated to find one suitable. Moreover, we need to alter the methodology of isolating and purifying the terpolymers in order to obtain cleaner NMR spectra. Once effectively purified, we believe we will achieve better film formation, in particular getting them to remain optically clear.

C. Structure III

Structure III with PEO or PEI HBs will be prepared according to Figure MG2. Each respective monomer will be polymerized from the PIB centerblock using appropriate ring-opening chemistries. The resulting triblock is then fitted with terminal alkyne groups using esterification. Then CuAAC will be used to place the outer PS blocks which have been fitted with azide terminal groups.

IV References

1. Kopchick, J.G.; Storey, R.F.; Jarrett, W.L.; Mauritz, K.A. *Polymer* 2008, 49, 5045-5052.
2. Kopchick, J.G. Ph.D. Dissertation, The University of Southern Mississippi, Hattiesburg, MS, 2006.